

1016,379



# PATENT SPECIFICATION

NO DRAWINGS

1016,379

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Int. Cl.: C07F // C01B, C08G

## COMPLETE SPECIFICATION

### The Preparation of Compounds containing a Substituted Dodecahydrododecaborate Anion

We, E.I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

This invention relates to the preparation of compounds containing substituted dodecahydrododecaborate anions.

We have found that the hydrogen atoms in the dodecahydrododecaborate anion,  $(B_{12}H_{12})^{2-}$ , can be successively replaced by reacting the acid hydrate  $H_2B_{12}H_{12}\cdot nH_2O$  with an epoxide. Therefore, we provide according to the present invention a process for preparing boron compounds which comprises reacting an epoxide with  $H_2B_{12}H_{12}\cdot nH_2O$ .

By varying the relative quantities of the two reactants, anions are obtained having the formula  $[B_{12}H_{12-y}(OR)_y]^{2-y}$  where y is an integer, generally from 1 to 4, and OR is the monovalent radical formed by the ring opening of the epoxide. The OR is directly bonded to the boron in the borate cage structure through the oxygen atom.

By conducting the reaction in a solution of  $H_2B_{12}H_{12}\cdot nH_2O$  and regulating the temperature to provide a controlled reaction rate, high yields of substituted hydrodecaborate anions are produced. The product is conveniently recovered by precipitation as an insoluble salt, for example, the cesium salt.

The substituted polyhedral boron compounds produced in this process have a cage structure. The (2-) charge associated with the anion is based on the charge on the boron cage, independently of the —OR groups present. However, there may be electrical charges arising from the nature of the R groups in addition to the charge associated with the polyhedral borane cage. For example, R may bear carboxyl groups which, in ionic form, require the presence of a cation. As a further illustration, R may bear basic groups, e.g.,  $NH_2$ , which will form ionizable salts with acids. Cations and anions derived from R groups are considered to be part of these groups and are included within the scope of the definition of R.

In carrying out the process  $H_2B_{12}H_{12}\cdot nH_2O$  is conveniently used in the form of an aqueous syrup in which water and  $H_2B_{12}H_{12}\cdot nH_2O$  are present in equal amounts by weight. However, no water is necessary for the present process beyond that which is necessary to permit the dodecahydrododecaborate (2-) anion to be in its acidic form.

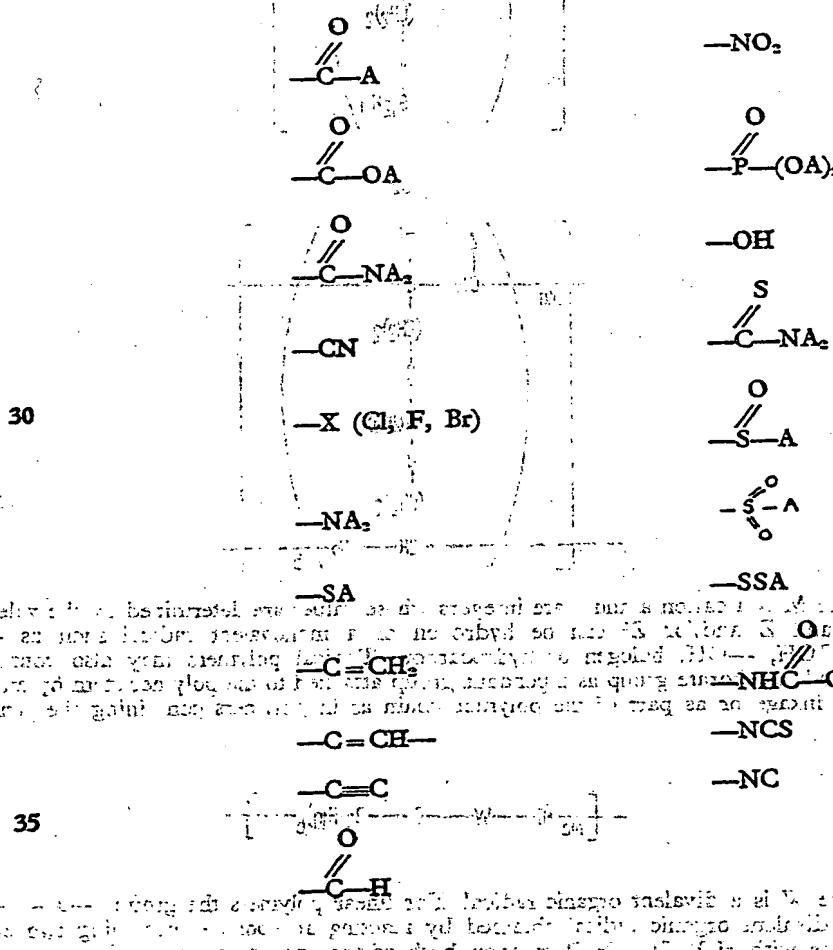
In a preferred procedure the  $H_2B_{12}H_{12}\cdot nH_2O$  aqueous syrup mentioned is mixed with a solvent such as glyme (1,2-dimethoxyethane) to form a solution, and an epoxide in liquid form (i.e., a liquid epoxide, or a solid epoxide in solution) is added slowly (usually dropwise) while maintaining the temperature of the reaction mixture within the range necessary to achieve the desired reaction rate. The reaction is practically instantaneous and is controlled by the rate of addition of the epoxide and by regulating the solution temperature. With very highly reactive epoxides, temperatures of  $0^\circ C$ . and even lower may be necessary for reaction rate control whereas temperatures above  $30^\circ C$ . may be used to increase the reaction rate of relatively sluggish epoxides. For many epoxides a range of  $10^\circ$  to  $30^\circ C$ . is useful. Untried epoxides may be handled by starting the reaction at a low temperature and gradually warming the reaction mixture until the desired reaction rate is achieved. The reaction product is readily recovered

by precipitation as an insoluble salt, by any convenient recovery procedure such as extraction, distillation and the like may be used. Cesium in the form of CsF and CsOH is preferred as the precipitating agent.

Both liquid and solid epoxides may be utilized in this invention. Solid epoxides are conveniently dissolved in a solvent miscible with the  $H_2B_{12}H_{12}nH_2O$  solution to be used in order to facilitate contact between the reactants. Usually both reactants can be dissolved in glyme which is accordingly a preferred solvent for practicing this invention. Preferably the solvent used is one in which  $H_2B_{12}H_{12}nH_2O$  dissolves readily. Most desirably the solvent should also permit recovery of the product by a convenient method.

The process may be practiced with any epoxide. When there are two or more oxirane groups in the epoxide, these may be vicinal or may be separated by one or more intervening atoms and may be mono- or poly-functional, cyclic or acyclic. Polymeric products are obtainable by using appropriate epoxides, that is, epoxides with polymer forming functional groups or epoxides which are already polymers containing one or more epoxy groups. Epoxides containing ethylenic unsaturation sometimes react with  $H_2B_{12}H_{12}nH_2O$  to produce compounds in which —OR, the epoxide compound moiety, is saturated. Otherwise the organic portion of the reaction product usually corresponds to the epoxide reagent used, the epoxy group simply opening up and attaching to boron in the boron hydride cage by an ether-like linkage.

The groups which are joined to the epoxide ring carbons may be the same as or different to each other and may be, for example, hydrogen or a hydrocarbon group such as an aromatic, aliphatic or alicyclic group or a heterocyclic group or may be a functional group such as one of the functional groups listed below or one of the above-mentioned groups substituted with one or more of the following functional groups:



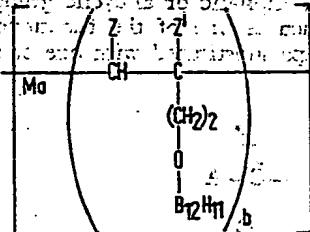
In the above group A is a monovalent organic radical preferably hydrocarbon, of at most about 18 carbons, which can be alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl and the like. Any of the groups on the epoxide ring may contain one or more epoxy groups and any two or more of them together may in combination represent an aromatic, alicyclic or heterocyclic ring or group.

The preferred epoxides are those in which the epoxide ring carbons are each attached to the hydrogen atom and to one other group.

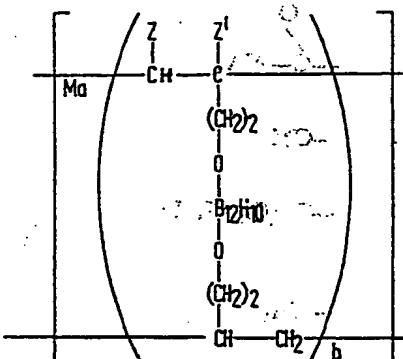
Polymer-forming groups attached to the epoxide ring may be capable of forming addition polymers or condensation polymers. Following reaction of the particular epoxide with  $H_2B_{12}H_{12}\cdot nH_2O$ , the polymer may be produced by a suitable polymerisation reaction.

Polymers containing the hydrododecaborate anion may also be prepared by the process of the present invention by employing a polymer containing an epoxy group. The polymer may be an addition or a condensation polymer and is preferably a linear polymer. Polyamides, polyesters and polyureas are preferred condensation polymers, being very useful for the formation of fibers and films, coatings, finishes and insulation in applications where the presence of the hydrododecaborate anion is desirable.

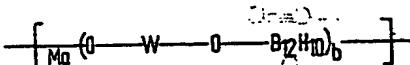
The polymers of this invention contain the hydrododecaborate group, usually as a component of each recurring unit. This group may be in the stem of the polymer chain or a pendant group. Thus typical addition polymers have the recurring unit



or



where M is a cation and b are integers whose values are determined by the valence of M, and Z and/or Z' can be hydrogen or a monovalent radical such as  $-CN$ ,  $-COOH$ ,  $-OH$ , halogen or hydrocarbon. Typical polymers may also contain the hydrododecaborate group as a pendant group attached to the polymer stem by an ether-like linkage or as part of the polymer chain as in polymers containing the structural unit



where W is a divalent organic radical. For linear polymers the group  $-O-W-O-$  is a divalent organic radical obtained by reacting an epoxide containing two epoxide groups with  $H_2B_{12}H_{12}\cdot nH_2O$  to open both of the epoxide groups. When the epoxide

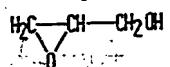
used contains more than two epoxide groups cross linking will usually result if more than two of the epoxide groups in it are reactive under the conditions used.

The preferred W groups are hydrocarbon radicals, polyalkylene ether radicals and fluorosubstituted alkylene radicals.

All of the polymers referred to may have molecular weight comparable to those of any conventional and well known polymers. Persons skilled in polymer chemistry are well aware of the reaction conditions which govern polymer formation and size and will have no difficulty in producing in accordance with this invention polymers suitable for particular applications and requiring specific properties in addition to those unique properties contributed by boron.

Other epoxides useful in this invention include the following:

Glycidol



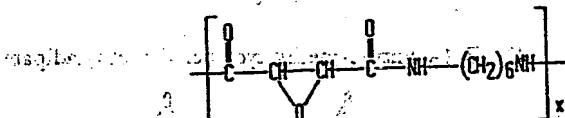
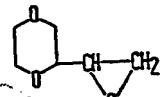
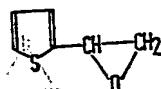
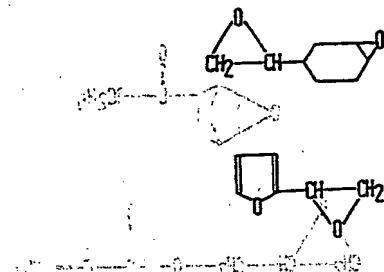
Vinyl cyclohexane diepoxyde

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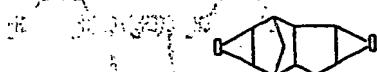
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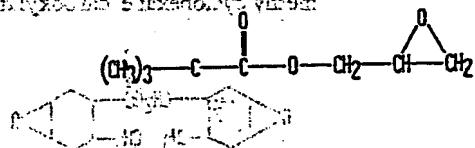
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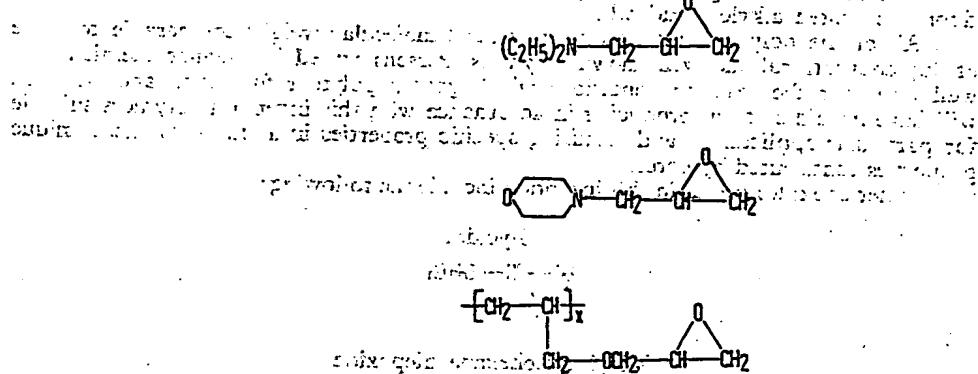
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*2-epoxy-3-(1-phenyl-1-oxido-2-propyl)-3-oxo-1-phenylpropanoate*



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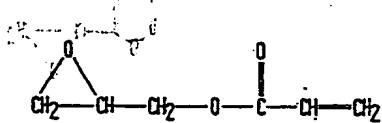
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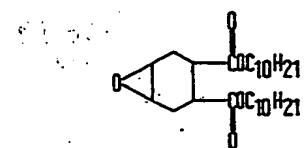
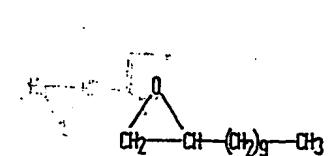
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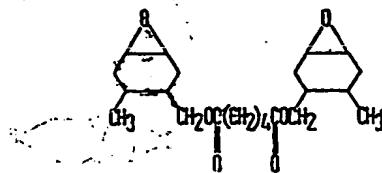
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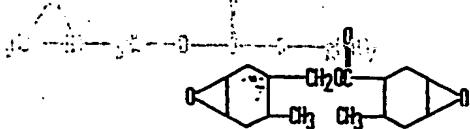
### Di-(3,4-epoxy-6-methylcyclohexyl-methyladipate)



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### 3,4-Epoxy-6-methylcyclohexyl-methyl-3,4-epoxy-6-methylcyclohexane carboxylate

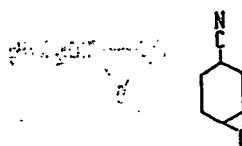
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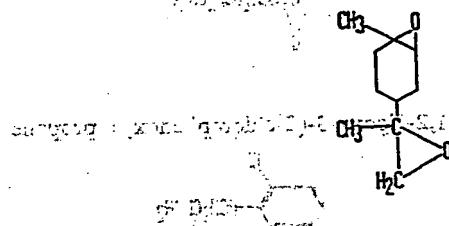
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## 3,4-Epoxycyclohexane carbonitrile

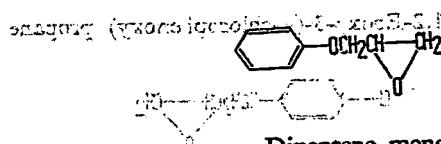


see drawing (3,4-epoxycyclohexylidene)-1-cyano-2-ol

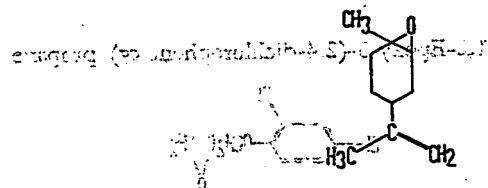
## Dipentene dioxide (limonene dioxide)



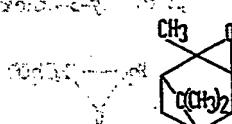
## 1,2-Epoxy-3-phenoxy propane



## Dipentene monoxide



## Alpha pinene oxide



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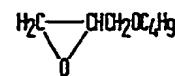
## 1,2-Epoxy-3-allyloxy propane



## see drawing (3,4-Epoxy-3-(4-allylphenoxy) propanoate)



## 1,2-Epoxy-3-butoxy propane

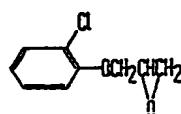


## 1,2-Epoxy-3-(2-chloroethoxy) propane



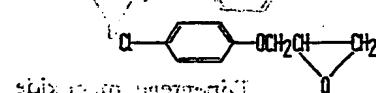
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## 1,2-Epoxy-3-(2-chlorophenoxy) propane

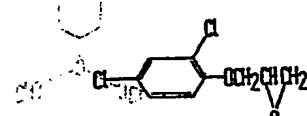


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## 1,2-Epoxy-3-(4-chlorophenoxy) propane



## 1,2-Epoxy-3-(2,4-dichlorophenoxy) propane



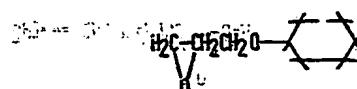
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## 1,2-Epoxy-3-ethoxypropane

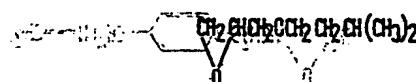


## 1,2-Epoxy-3-cyclohexyloxypropane



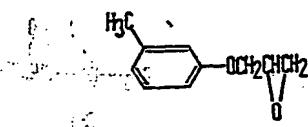
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## 1,2-Epoxy-3-(3-methylbutoxy) propane

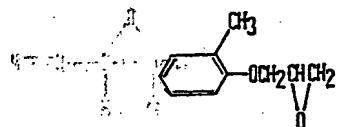


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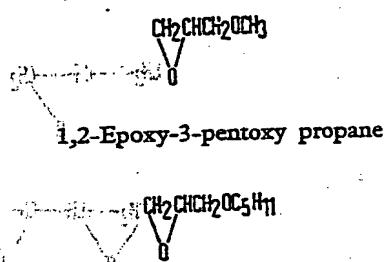
## 1,2-Epoxy-3-(3-methylphenoxy) propane



## 1,2-Epoxy-3-(2-methyl phenoxy) propane



## 1,2-Epoxy-3-methoxy propane



100% racemic epoxide. In addition to the above, 1,2-Epoxy-3-propoxy propane, also having a 10% excess of one enantiomer, was found to be formed. This epoxide is believed to be formed by a similar mechanism as the above epoxides, except that the epoxidation step is based on the reaction of the epoxide with a chiral reagent.

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## Phenyl methyl glycidic ester

Another epoxidation product was found to be 1,2-Epoxy-3-(3-methoxyphenyl) propanoate. This epoxide was formed by the reaction of 1,2-Epoxy-3-(3-methoxyphenyl) propanoate with a chiral reagent.

## 3,4-Epoxy-2,5-dihydrothiophene-1,1-dioxide

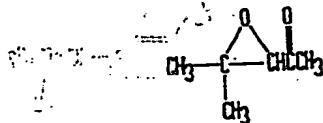


This epoxide was formed by the reaction of 1,2-Diphenyl ethylene oxide with a chiral reagent. The epoxide was formed in 100% yield.

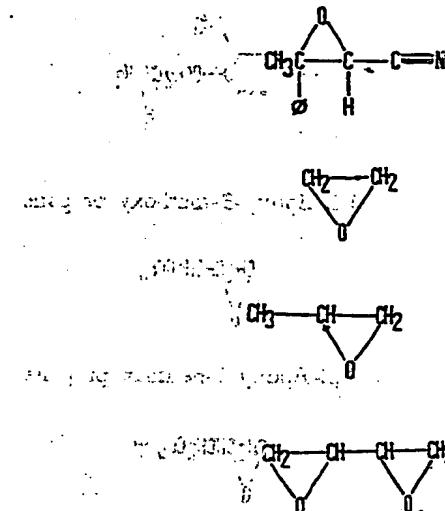
The epoxide was formed in 100% yield by the reaction of 1,2-Diphenyl ethylene oxide with a chiral reagent.

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## 3,4-Epoxy-4-methyl-2-pentanone



## 3-Phenyl-2,3-epoxy-butyronitrile



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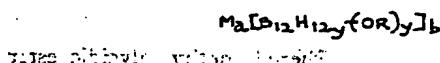
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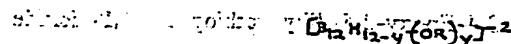
In the above structural formulas  $x$  is a whole number, usually a large whole number, signifying the number of recurring structural groups in the formula of a polymer and  $\varnothing$  represents a phenyl group.

The salts corresponding to the borate anions have the generic formula:—



where  $M$  is a cation and  $a$  and  $b$  are positive whole numbers of 1—3 inclusive, whose values are determined by the valence of  $M$ . The —OR groups, when more than one is present, may be the same or different. Where R is a polymeric radical the above formula would represent a recurring unit in the polymer.

The boron-containing group



in the above formula forms an anion in aqueous solution and behaves as a stable chemical entity in conventional reactions. By varying the amount of epoxide used in the process of preparation,  $y$  may be varied as desired to produce  $(B_{12}H_{12}OR)^{-2}$ ,  $[B_{12}H_{10}(OR)]^{-2}$ ,  $[B_{12}H_8(OR)]^{-3}$ ,  $[B_{12}H_6(OR)]^{-4}$  and higher substituted boron cage anions of this type. Since these anions exhibit detergent properties in aqueous solution the compounds containing more than two (OR) groups are difficult to recover. Anions of the general formula are conveniently recovered as their insoluble salts such as the cesium salt  $Cs_2B_{12}H_{12-y}(OR)_y$ .

$M$  may be any cation which forms a salt with the  $[B_{12}H_{12-y}(OR)]^{-2}$  in the reaction product mixture. Where recovery of the boron derivative is not desired, as when it is going to be used in solution, then  $M$  may be any cation which produces a salt of the

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desired solubility with the anion produced. Exemplary cations include the following: hydrogen, hydronium ( $H_3O^+$ ), a metal ammonium ( $MNH_4^+$ ), hydrazonium ( $NH_5^+$ ), N-substituted ammonium, N-substituted hydrazonium, aryl diazonium, pyridinium, quinolinium, sulfonium, phosphonium, and metal amines.

More specifically, M can be lithium, sodium, cesium, beryllium, barium, lanthanum, zirconium, vanadium, manganese, iron, cobalt, copper, zinc, mercury, aluminum, thallium, tin, lead, antimony, bismuth, silver or any other metal.

As further more specific examples M can be  $ANH_3^+$ ,  $A_2NH_2^+$ ,  $A_3NH^+$ ,  $A_4N^+$ ,  $(ANHNH_2)^+$ ,  $(A_2N-NH_2)^+$ ,  $A_2S^+$  or  $A_2P^+$ , where A is an organic radical bonded to the nitrogen, sulfur or phosphorus. The A groups are not critical features of these cation groups. The substituents represented by A can be open-chain or closed-chain, saturated or unsaturated, or the groups can be composed of heterocyclic rings of which the nitrogen, sulfur or phosphorus is a component, e.g., pyridine, quinoline, morpholine or hexamethylenimine. Preferably A, for reasons of availability of reactants, represents

15 a hydrocarbon group of at most 18 carbons.

The group M can be a Werner-type coordination complex, e.g., a metal ammine such as  $[Ni(NH_3)_6]^{2+}$ ,  $[Zn(NH_3)_4]^{2+}$ ,  $[CO(NH_3)_5CH_3]^{2+}$  and  $[CO(NH_3)_6]^{2+}$ . The products of this invention may be used *in situ* or may be recovered and purified by any convenient means. Crystallization from aqueous ethanol solutions is usually effective. For products of limited stability, solutions of the products can be treated with absorptive agents, e.g., activated charcoal or silica gel to adsorb the major portion of the impurities.

20 The processes which have been described can be employed to obtain compounds having one or more —OR groups. These groups, if more than one is present, can be alike or different. To obtain compounds having two or more —OR groups which are

25 unlike, the dodecahydrododecaborate acid hydrate is reacted with one epoxide until the desired number of substituents are introduced and the partially substituted product is then reacted with a second epoxide. The intermediate partially substituted product can, if desired, be isolated prior to reaction with the second epoxide. The process can be repeated with a third epoxide or even further. Further modification of various substituent groups can be accomplished by conventional methods to obtain compounds having a broad range of OR groups.

30 The salts produced by the process of this invention are usually solids, many of which dissolve in water. They vary in stability, and certain nitro and nitroso containing compounds are sensitive to shock and should be kept moist while handling. Others, including the halogen-substituted products and hydrocarbon-substituted products, are stable and can be stored for long periods without extraordinary care.

35 The invention provides a useful method for introducing the boron cage structure into organic compounds with its attendant properties into polymers. As pointed out above, this is accomplished by utilising epoxides having polymer forming functional groups or other groups convertible into such polymer forming groups. Polymers containing one or more epoxide groups may also be used. The process is also useful for introducing the hydrododeca-

40 borate anion into a wide variety of other compounds for applications where a high boron content is desirable. Many of the compounds have detergent properties and some are coloured permitting their use as pigments or dyes. The dodecaborate cage of the products of this invention possess an aromatic character and undergoes reactions in a manner resembling benzene, that is, it will react with reagents to add substituents which are capable of bonding to a carbon of an aromatic nucleus such as benzene, naphthalene or toluene. Thus, compounds or anions produced by this invention and in

45 which the boron cage hydrogen atoms are not completely replaced by OR groups, may be reacted with the numerous reagents suitable for reaction with an aromatic compound to produce an endless variety of compounds suitable for predetermined end uses. The process of this invention and products produced thereby are illustrated in the following examples. The preparation of  $Na_2B_{12}H_{12} \cdot 2H_2O$  from diborane is also shown.

#### EXAMPLE I

##### A. Preparation of $M_2B_{12}H_{12} \cdot 2H_2O$ (where M is $Na^+$ )

50 A pressure vessel of 400 ml. capacity is charged with 9.5 g. of sodium hydroborate and 75 ml. of 1,2-dimethoxyethane, also called "glyme". The vessel is closed, cooled to  $-80^\circ C$ . and evacuated to a pressure of about 0.001 mm. f mercury. Diborane (14.0 g.) is charged into the vessel which is then sealed and heated with agitation under autogenous pressure for 16 hours at  $120^\circ C$ . The molar ratio of  $NaBH_4$  to  $B_2H_6$  in this reaction is 1:2. The reactor is cooled; the volatile products are released by venting

and the contents of the tube are washed into a receiver with glyme. A suspension of a white solid in a yellow liquid is formed from which the solid is separated by filtration. The solid is dissolved in hot tetrahydrofuran and the solution is filtered to remove a trace of unreacted sodium hydroborate. The hot filtrate is diluted with glyme and chilled to yield 14.0 g. of disodium polyhydropolyborate ( $2^-$ ) as long, glistening white needles. The compound crystallizes with 1,2-dimethoxyethane and water. The compound has the following infrared absorption frequencies:  $2.8\mu$ , sharp, medium;  $3.9\mu$  with  $4.02\mu$  shoulder, sharp, strong;  $6.2$ ,  $7.8$  and  $8.4\mu$ , sharp, medium;  $9.3\mu$ , medium, sharp, strong;  $10.9\mu$ , sharp, strong; and  $13.9\mu$ , broad, weak. The compound shows the following elemental analysis: Analysis Found: C, 14.33; H, 7.09; B, 45.08; Na, 16.1. The compound therefore is a solvate of disodium dodecahydrododecaborate having the following composition:

15  $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 0.86\text{C}_2\text{H}_6\text{O}_2 \cdot 1.25\text{H}_2\text{O}$ . The compound can be obtained as its hydrate, free of ether of solvation, by recrystallization from a large quantity of diethyl ether or tetrahydrofuran/diethyl ether mixtures, followed by drying under reduced pressure. The ether-free hydrate has infrared absorption characteristics as follows:  $2.8\mu$ , sharp, medium;  $3.9\mu$ , sharp, strong;  $6.2\mu$ , sharp, medium;  $9.25\mu$ , sharp, medium; and  $13.9\mu$ , broad, medium. The elemental analysis is as follows: Found: H, 6.56; B, 62.02; Na, 20.5.

The compound is therefore a monohydrate of disodium dodecahydrododecaborate, i.e.,  $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot \text{H}_2\text{O}$  (calculated analysis: H, 6.85; B, 63.05; Na, 22.32).

20 The dihydrate,  $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 2\text{H}_2\text{O}$ , is obtained in the above process by less intensive drying of the crystals.

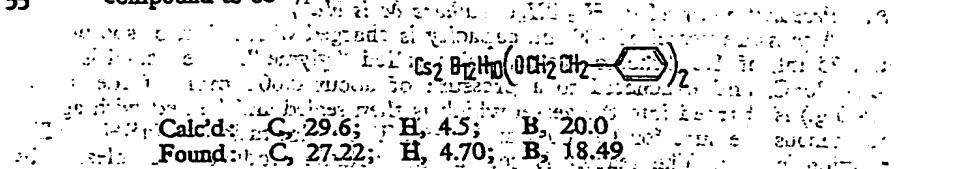
25 **Preparation of  $\text{H}_2\text{B}_{12}\text{H}_{12} \cdot n\text{H}_2\text{O}$** . A solution of 2.9 g. of  $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 2\text{H}_2\text{O}$ , obtained in Part A, in 30 ml. of water is passed through a 0.5 inch diameter chromatography column containing 80 ml. of a commercial acidic ion exchange resin ("Amberlite IR 120-H"). "Amberlite" is a trade mark. The water effluent is clear, colorless and acidic. The column is rinsed with more water until the effluent is no longer acidic and the water fractions are combined. Evaporation of the combined aqueous solutions under reduced pressure (1 mm. of mercury) at a temperature of about  $40^\circ\text{C}$ . leaves a white solid residue which has the formula  $\text{H}_2\text{B}_{12}\text{H}_{12} \cdot n\text{H}_2\text{O}$ .

30 **EXAMPLE 2**. A solution of 2.9 g. (0.013 mole) of  $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 2\text{H}_2\text{O}$  in 10 ml. of water is passed through an "Amberlite IR 120-H" ion exchange column to produce the acid  $\text{H}_2\text{B}_{12}\text{H}_{12} \cdot n\text{H}_2\text{O}$ . Water is evaporated in vacuum at  $<25^\circ\text{C}$ . and the solid residue dissolved in 20 ml. of glyme. A solution of 2.4 g. (0.026 mole) of epichlorohydrin in 10 ml. of glyme is added dropwise. The reaction is cooled in an ice bath. The solvent is evaporated in vacuum and the residue dissolved in ethanol. Addition of 3.9 g. (0.026 mole) of CsF dissolved in 10 ml. of glyme results in the formation of a white precipitate.

35 Analysis shows that one molecule of solvent has also reacted to give a diether,  $\text{CsB}_{12}\text{H}_{10}(\text{OCH}_2\text{CH}_2\text{Cl})(\text{OCH}_2\text{CH}_2\text{OCH}_3)$ .

40 **Calcd.**: C, 12.5; H, 4.0; B, 22.7; Cl, 6.2. **Found:** C, 11.27; H, 3.86; B, 20.67; Cl, 6.67.

45 **EXAMPLE 3**. To a solution of  $\text{H}_2\text{B}_{12}\text{H}_{12} \cdot n\text{H}_2\text{O}$  in glyme, prepared as in Example 2, is added dropwise 2.7 g. (0.026 mole) of styrene oxide while cooling in an ice bath. Temperature is maintained at  $35$ – $40^\circ\text{C}$ . The solvent is evaporated in vacuum to give a yellow gum. This residue is dissolved in 20 ml. of ethanol and 3.9 g. (0.026 mole) of CsF dissolved in ethanol is added. A white precipitate results. The precipitate is purified by washing with ethanol and ethyl ether. Elemental and infrared analyses show the compound to be



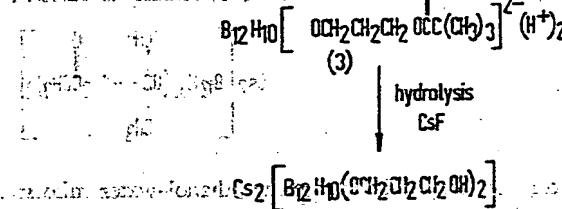
EXAMPLE 4  
A solution of 2.0 g. (0.013 mole) of dicyclopentadiene dioxide dissolved in 10 ml. of glyme is added dropwise to a 20 ml. solution of  $H_2B_{12}H_{12}nH_2O$  in glyme prepared as in Example 2. The solution is maintained at 40°C. by cooling with an ice bath. The solution is allowed to cool to room temperature and the solvent is evaporated at reduced pressure. The residual tar is dissolved in ethanol and a solution of 3.9 g. (0.026 mole) of CsF added. A light tan precipitate forms and is isolated. Elemental and infrared analyses show the product is



Calcd: C, 12.3; H, 3.67; B, 21.6  
Found: C, 13.02; H, 4.54; B, 24.62

## EXAMPLE 5

This example illustrates the following reaction:  
A solution of 2.0 g. (0.013 mole) of dicyclopentadiene dioxide dissolved in 10 ml. of glyme is added dropwise to a 20 ml. solution of  $H_2B_{12}H_{12}nH_2O$  in glyme prepared as in Example 2. The solution is maintained at 40°C. by cooling with an ice bath. The solution is allowed to cool to room temperature and the solvent is evaporated at reduced pressure. The residual tar is dissolved in ethanol and a solution of 3.9 g. (0.026 mole) of CsF added. A light tan precipitate forms and is isolated. Elemental and infrared analyses show the product is



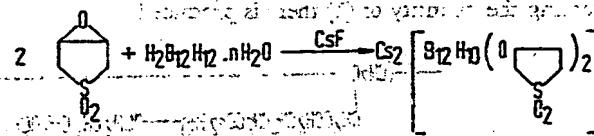
## EXAMPLE 6

The procedure of Example 2 is followed and the ultimate product anion (4) is recovered by precipitation and identified by elemental and infrared analyses as the cesium salt  $Cs_2B_{12}H_{10}(OCH_2CH_2CH_2OH)_2$ .

Calcd: C, 7.5; H, 3.7; B, 27.0  
Found: C, 9.05; H, 3.79; B, 22.87

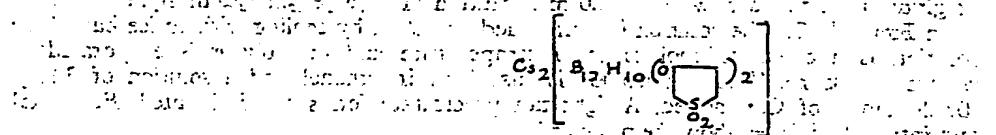
## EXAMPLE 6

The following reaction is carried out:



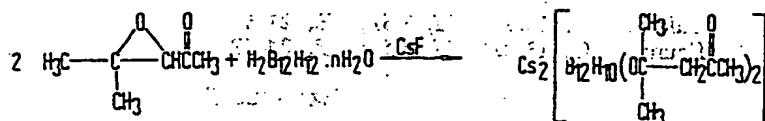
A solution of 22.4 g. (0.10 mole) of  $Na_2B_{12}H_{12}2H_2O$  in 40 ml. of water is passed through an "Amberlite IR 120-H" ion exchange column to produce the acid  $H_2B_{12}H_{12}nH_2O$ . Water is evaporated from the  $H_2B_{12}H_{12}nH_2O$  in vacuum at 20°C. to give a white solid residue. The acid residue is dissolved in 60 ml. of glyme and 26.8 g. (0.20 mole) of 3,4 - epoxy - 2,5 - dihydrothiophene - 1,1-dioxide added dropwise. Glyme is evaporated in vacuum and the residue dissolved in 60 ml. of ethanol. A solu-

tion of 30.4 g. (0.20 mole) of cesium fluoride in 60 ml. of ethanol is added to precipitate.

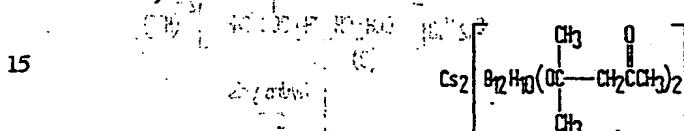


Product is recrystallized from an ethanol-water mixture.

**EXAMPLE 7**  
The following reaction is carried out:



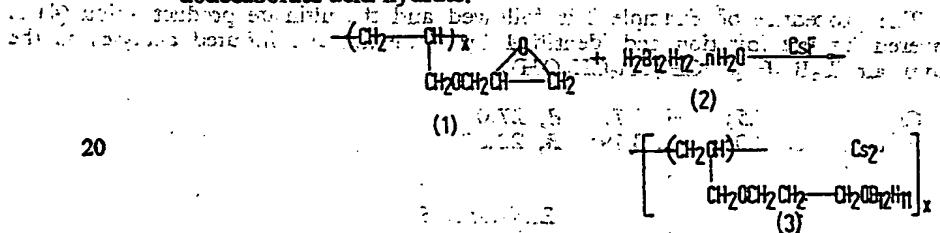
A solution of 22.4 g. (0.10 mole) of  $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot2\text{H}_2\text{O}$  in 40 ml. of water is passed through an "Amberlite IR 120-H" ion exchange column to produce the acid  $\text{H}_2\text{B}_{12}\text{H}_{12}\cdot\text{nH}_2\text{O}$ . Water is evaporated from the  $\text{H}_2\text{B}_{12}\text{H}_{12}\cdot\text{nH}_2\text{O}$  in vacuum at 20°C. to give a solid residue. The acid residue is dissolved in 60 ml. of glyme and 22.8 g. (0.20 mole) of 3,4-epoxy-4-methyl-2-pentanone added dropwise. Glyme is evaporated in vacuum and the residue dissolved in 60 ml. of ethanol. A solution of 30.4 g. (0.20 mole) of cesium fluoride in 60 ml. of ethanol is added to precipitate



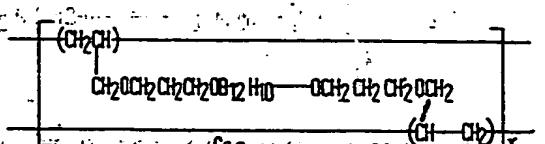
Product is recrystallized from an ethanol-water mixture.

### EXAMPLE 8

This example illustrates the reaction of a polymeric epoxide with dodecahydro-dodecaborate acid hydrate.



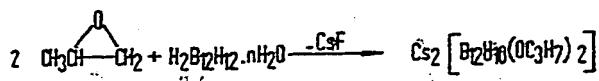
The procedure of Example 2 is followed to produce the product (3) shown. By increasing the quantity of (1) there is produced:



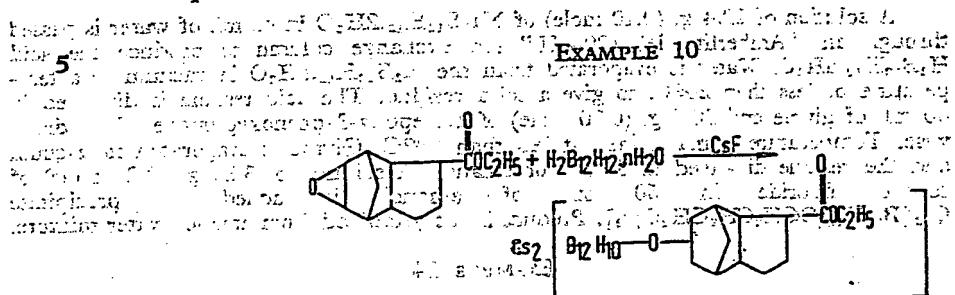
which was characterized by elemental and infrared analyses to have the structure shown.

Calcd.: B, 20.4% at ambient temp. & 1T ambient light. Found: B, 18.4% (dried, 100°C - 1 atm). C, 16.6% (dried, 100°C - 1 atm).

## EXAMPLE 9

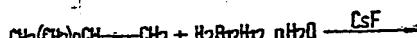


The reaction is conducted according to the procedure of Example 2 in glyme at a temperature of 30°C. and the product recovered as its cesium salt.



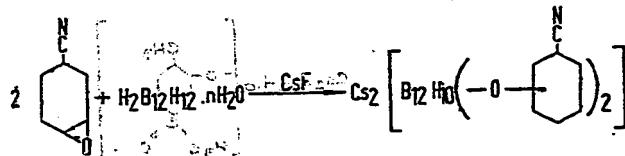
The procedure of Example 2 is followed at a temperature of 30°C. in glyme. The product is precipitated and recovered as its cesium salt.

## EXAMPLE 11

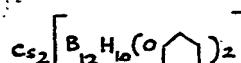


Reaction mixture to form 2 mol CH<sub>2</sub>(CH<sub>2</sub>)CH<sub>2</sub>B<sub>12</sub>H<sub>10</sub> (start Cs<sub>2</sub>) is added to 2 mol 3,4-epoxycyclohexane and 1 mol Cs<sub>2</sub> in glyme at a temperature of less than 30°C. The reaction mixture is stirred until the reaction is complete. The product is isolated by adding 1 mol Cs<sub>2</sub> to the reaction mixture. After stirring for 1 hr, the reaction mixture is filtered off the solid Cs<sub>2</sub>. The filtrate is concentrated to dryness. The residue is dissolved in 10 ml. of ethanol and 10 ml. of water. The resulting solution is cooled to -78°C. and 10 ml. of diethyl ether is added. The resulting precipitate is collected and washed with diethyl ether. The final product is dried in a vacuum desiccator.

## EXAMPLE 12



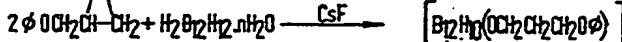
A solution of 22.4 g. (0.10 mole) of Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub>·2H<sub>2</sub>O in 40 ml. of water is passed through an "Amberlite IR 120-H" ion exchange column to produce H<sub>2</sub>B<sub>12</sub>H<sub>12</sub>·nH<sub>2</sub>O. Water is evaporated from the H<sub>2</sub>B<sub>12</sub>H<sub>12</sub>·nH<sub>2</sub>O in vacuum at a temperature of less than 20°C. to give a solid residue. The acid residue is dissolved in 60 ml. of glyme and 24.6 g. (0.20 mole) of 3,4-epoxycyclohexane carbonitrile added dropwise. Temperature is maintained at less than 30°C. Glyme is evaporated in vacuum and the residue dissolved in 60 ml. of ethanol. A solution of 30.4 g. (0.20 mole) of cesium fluoride in 60 ml. of ethanol is added to precipitate.



Reaction mixture to form 2 mol C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>B<sub>12</sub>H<sub>10</sub> (start Cs<sub>2</sub>) is added to 2 mol 3,4-epoxycyclohexane carbonitrile and 1 mol Cs<sub>2</sub> in glyme at a temperature of less than 30°C. The reaction mixture is stirred until the reaction is complete. The product is isolated by adding 1 mol Cs<sub>2</sub> to the reaction mixture. After stirring for 1 hr, the reaction mixture is filtered off the solid Cs<sub>2</sub>. The filtrate is concentrated to dryness. The residue is dissolved in 10 ml. of ethanol and 10 ml. of water. The resulting solution is cooled to -78°C. and 10 ml. of diethyl ether is added. The resulting precipitate is collected and washed with diethyl ether. The final product is dried in a vacuum desiccator.

Product is recrystallized from an ethanol-water mixture.

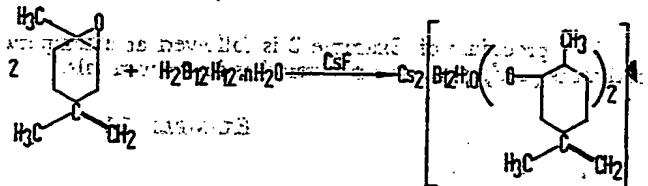
## EXAMPLE 13



5 A solution of 22.4 g. (0.10 mole) of  $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot 2\text{H}_2\text{O}$  in 40 ml. of water is passed through an "Amberlite IR 120-H" ion exchange column to produce the acid  $\text{H}_2\text{B}_{12}\text{H}_{12}\text{nH}_2\text{O}$ . Water is evaporated from the  $\text{H}_2\text{B}_{12}\text{H}_{12}\text{nH}_2\text{O}$  in vacuum at a temperature of less than  $20^\circ\text{C}$ .

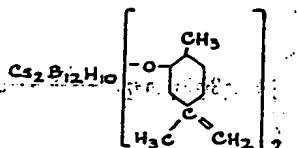
10 To residue is dissolved in 60 ml. of glyme and 30.0 g. (0.20 mole) of 1,2-epoxy-3-phenoxypropane added dropwise. Temperature is maintained at less than  $30^\circ\text{C}$ . Glyme is evaporated in vacuum and the residue dissolved in 60 ml. of ethanol. A solution of 30.4 g. (0.20 mole) of cesium fluoride in 60 ml. of ethanol is added to precipitate  $\text{Cs}_2[\text{B}_{12}\text{H}_{10}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{O})_2]$ . Product is recrystallized from ethanol-water mixture.

## EXAMPLE 14



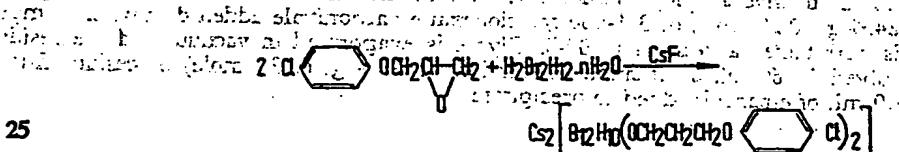
15 A solution of 22.4 g. (0.10 mole) of  $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot 2\text{H}_2\text{O}$  in 40 ml. of water is passed through an "Amberlite IR 120-H" ion exchange column to produce the acid  $\text{H}_2\text{B}_{12}\text{H}_{12}\text{nH}_2\text{O}$ . Water is evaporated from the  $\text{H}_2\text{B}_{12}\text{H}_{12}\text{nH}_2\text{O}$  in vacuum at a temperature of less than  $20^\circ\text{C}$ .

20 To residue is dissolved in 60 ml. of glyme and 30.4 g. (0.20 mole) of dipentene monoxide added dropwise. Temperature is maintained at less than  $0^\circ\text{C}$ . Glyme is evaporated in vacuum and the residue dissolved in 60 ml. of ethanol. A solution of 30.4 g. (0.20 mole) of cesium fluoride in 60 ml. of ethanol is added to precipitate.



Product is not recrystallized.

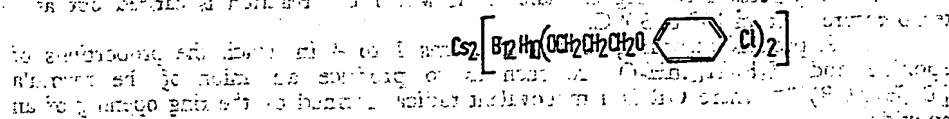
## EXAMPLE 15



25

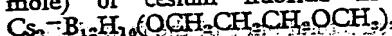
A solution of 22.4 g. (0.10 mole) of  $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot 2\text{H}_2\text{O}$  in 40 ml. of water is passed through an "Amberlite IR 120-H" ion exchange column to produce the acid  $\text{H}_2\text{B}_{12}\text{H}_{12}\text{nH}_2\text{O}$ . Water is evaporated from the  $\text{H}_2\text{B}_{12}\text{H}_{12}\text{nH}_2\text{O}$  in vacuum at  $20^\circ\text{C}$ .

(0.20 mole) of 1,2-epoxy-3-(4-chlorophenoxy)propane added dropwise. Glyme is evaporated in vacuum and the residue dissolved in 60 ml. of ethanol. A solution of 30.4 g. (0.2 mole) of cesium fluoride in 60 ml. of ethanol is added to precipitate

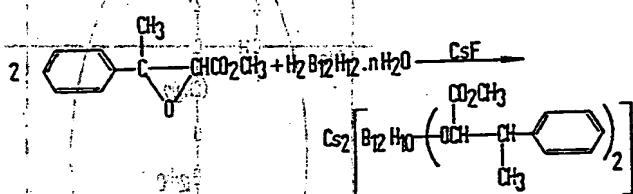


**EXAMPLE 16**

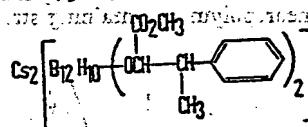
A solution of 22.4 g. (0.10 mole) of  $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot 2\text{H}_2\text{O}$  in 40 ml. of water is passed through an "Amberlite IR 120-H" ion exchange column to produce the acid  $\text{H}_2\text{B}_{12}\text{H}_{12}\cdot \text{nH}_2\text{O}$ . Water is evaporated from the  $\text{H}_2\text{B}_{12}\text{H}_{12}\cdot \text{nH}_2\text{O}$  in vacuum at 20°C. to give a solid residue. The acid residue is dissolved in 60 ml. of glyme and 38.4 g. (0.2 mole) of phenylmethylglycidic ester added dropwise. Glyme is evaporated in vacuum, and the residue dissolved in 60 ml. of ethanol. A solution of 30.4 g. (0.2 mole) of cesium fluoride in 60 ml. of ethanol is added to precipitate



**EXAMPLE 17**



A solution of 22.4 g. (0.10 mole) of  $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot 2\text{H}_2\text{O}$  in 40 ml. of water is passed through an "Amberlite IR 120-H" ion exchange column to produce the acid  $\text{H}_2\text{B}_{12}\text{H}_{12}\cdot \text{nH}_2\text{O}$ . Water is evaporated from the  $\text{H}_2\text{B}_{12}\text{H}_{12}\cdot \text{nH}_2\text{O}$  in vacuum at 20°C. to give a white solid residue. The acid residue is dissolved in 60 ml. of glyme and 38.4 g. (0.2 mole) of phenylmethylglycidic ester added dropwise. Glyme is evaporated in vacuum, and the residue dissolved in 60 ml. of ethanol. A solution of 30.4 g. (0.2 mole) of cesium fluoride in 60 ml. of ethanol is added to precipitate



**25**

Product is recrystallized from an ethanol-water mixture.

Our co-pending Patent Application No. 33447/63 (Serial 1016378) describes and claims a process for preparing the corresponding hydrodecaborates of the formula:  $\text{Ma}[\text{B}_{10}\text{H}_{10-n}(\text{OR})_n]$ .

**WHAT WE CLAIM IS:**

1. A process for preparing boron compounds which comprises reacting  $\text{H}_2\text{B}_{12}\text{H}_{12}\cdot \text{nH}_2\text{O}$  with an epoxide of benzimidazole.

2. A process according to claim 1 in which the reaction is carried out in a solution of  $\text{H}_2\text{B}_{12}\text{H}_{12}\cdot \text{nH}_2\text{O}$ .

3. A process according to claim 2 in which an epoxide in liquid form is added to a solution in 1,2-dimethoxy-ethane of a mixture of  $H_2B_{12}H_{12-n}H_2O$  and water in equal amounts by weight.

4. A process according to claim 3 in which the reaction is carried out at a temperature of from  $10^\circ$  to  $30^\circ C$ .

5. A process according to any of claims 1 to 4 in which the proportions of epoxide and  $H_2B_{12}H_{12-n}H_2O$  are such as to produce an anion of the formula  $[B_{12}H_{10}(OR)]^{2-}$  where OR is a monovalent radical formed by the ring opening of an epoxide.

10. 6. A process according to any of claims 1 to 5 in which the product is recovered from the reaction mixture by precipitation as an insoluble salt.

7. A process according to claim 6 in which the insoluble salt which is precipitated in the cesium salt.

15. 8. A process according to any of claims 1 to 7 in which the epoxide is ethylene oxide, propylene oxide or dicyclopentadiene dioxide.

9. A process according to any of claims 1 to 7 in which the epoxide contains a functional group which is capable of entering into a polymerisation reaction.

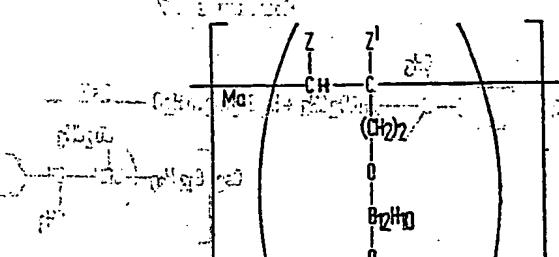
10. 10. A process according to any of claims 1 to 7 in which the epoxide is styrene oxide.

11. A process according to any of claims 1 to 7 in which the epoxide is a synthetic polymer containing an epoxide group.

12. A process for producing boron compounds substantially as herein described in any of Examples 2 to 17.

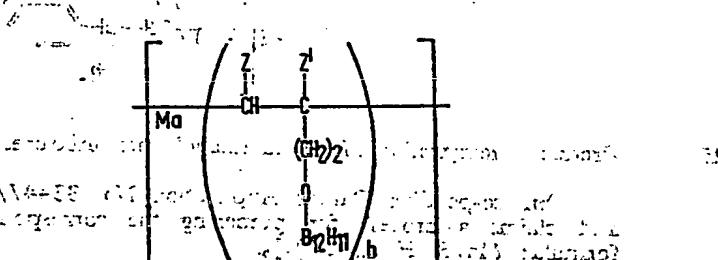
13. A boron compound when produced by a process claimed in any of the preceding claims.

25. 14. A linear polymer containing structural units of the formula: —



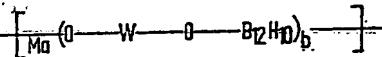
where M is a cation, Z and  $Z'$  are hydrogen or monovalent radicals and a and b are integers whose values are determined by the valence of M.

30. 15. A linear polymer containing structural units of the formula: —



where M is a cation, Z and  $Z'$  are hydrogen or monovalent radicals, and a and b are integers whose values are determined by the valence of M.

## 16. A polymer containing structural units of the formula



where M is a cation and a and b are integers whose values are determined by the valence of M and W is a divalent organic radical.

17. A polymer according to claim 16 in which W is a hydrocarbon radical, a polyalkylene ether radical or a fluorosubstituted alkylene radical.

18. A polymer containing a hydrodecaborate anion substantially as herein described.

19. A polymer containing a hydrodecaborate anion substantially as herein described in any of Examples 2 to 17.

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For the Applicants.

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